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*Sertifikaat*

REPUBLIEK VAN SUID AFRIKA

*Certificate*

REPUBLIC OF SOUTH AFRICA

*PATENT KANTOOR*
*DEPARTEMENT VAN HANDEL*
*EN NYWERHEID*

*PATENT OFFICE*
*DEPARTMENT OF TRADE AND*
*INDUSTRY*

Hiermee word gesertifiseer dat
This is to certify that

the documents annexed hereto are true copies of:

Application forms P.1, P2 and provisional specification of South African

Patent Application No. 2003/4632 as originally filed in the Republic of South

Africa on 13 June 2003 in the name of SASOL TECHNOLOGY (PTY)

LTD for invention entitled: "TRIMERISATION OF OLEFINS."

Geteken te in die Republiek van Suid-Afrika, hierdie dag van
**PRETORIA** 17th May 2004
Signed at in the Republic of South Africa, this day of

.......................................
Registrar of Patents

FORM P1
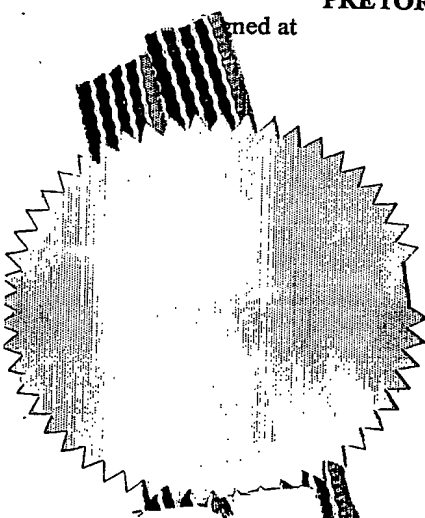
REPUBLIC OF SOUTH AFRICA
PATENTS ACT, 1978

## APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT

[Section 30 (1) - Regulation 22]

| | Revenue stamps or revenue franking machine impression |
|---|---|
| | Official date stamp |

The grant of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate

| | OFFICIAL APPLICATION NO. | | (i) | APPLICANT'S OR AGENT'S REFERENCE |
|---|---|---|---|---|
| 21 | 2003/4632 | | | F469 |

(ii) | FULL NAME(S) OF APPLICANT(S)
71 | SASOL TECHNOLOGY (PTY) LTD

(iii) | ADDRESS(ES) OF APPLICANT(S)
1 STURDEE AVENUE, ROSEBANK, 2196 JOHANNESBURG, SOUTH AFRICA

(iv) | TITLE OF INVENTION
54 | TRIMERISATION OF OLEFINS

(v) | The applicant claims priority as set out on the accompanying form P2.
The earliest priority claimed is          Country:          Number:          Date:

| (vi) | This application is for a patent of addition to Patent Application No. | 21 | 01 | |
|---|---|---|---|---|

| (vii) | This application is a fresh application in terms of section 37 and is based on Patent Application No. | 21 | 01 | |
|---|---|---|---|---|

(viii) This application is accompanied by:

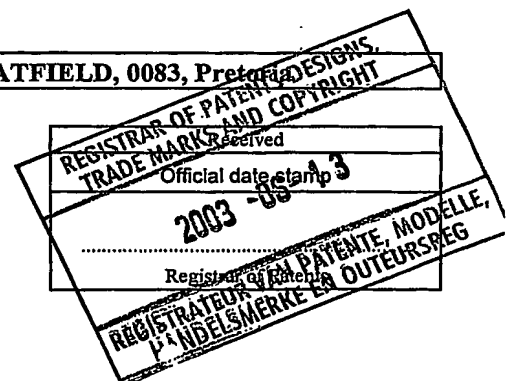| X | 1. | A single copy of a provisional or two copies of a complete specification of __16__ pages. |
|---|---|---|
| | 2. | Drawings of __ sheets |
| | 3. | Publication particulars and abstract (form P8 in duplicate). |
| | 4. | A copy of Figure __ of the drawings for the abstract. |
| | 5. | An assignment of invention. |
| | 6. | Certified priority document(s) (state number): |
| | 7. | Translation of the priority document(s). |
| | 8. | An assignment of priority rights. |
| | 9. | A copy of the form P2 and the specification of SA Patent Application No.   `21 | 01` |
| | 10. | A declaration and power of attorney form P3. |
| | 11. | Request for ante-dating on form P4. |
| | 12. | Request for classification on form P9. |
| | 13. | In terms of section 31(1) the applicant has added additional revenue stamps to this form for claiming priority after 12 months but before 15 months from the priority filing date. |
| X | 14. | Form P2 + copy |

(ix) | 74 | Address for service:     HAHN & HAHN INC, 222 Richard Street, HATFIELD, 0083, Pretoria

Dated this __13__ day of __June__ 20__03__

..........................................................
Signature of applicant(s) or agent

This duplicate will be returned to the applicant's address for service as proof of lodging but is not valid unless endorsed with an official stamp

# REGISTER OF PATENTS

| OFFICIAL APPLICATION NO. | LODGING DATE: PROVISIONAL | ACCEPTANCE DATE |
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| INTERNATIONAL CLASSIFICATION | LODGING DATE: COMPLETE | GRANTED DATE |
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**FULL NAME(S) OF APPLICANT(S)/PATENTEE(S)**

71

## SASOL TECHNOLOGY (PTY) LTD

| APPLICANTS SUBSTITUTED: | | DATE REGISTERED |
|---|---|---|
| 71 | | |

| ASSIGNEE(S) | | DATE REGISTERED |
|---|---|---|
| 71 | | |

**FULL NAME(S) OF INVENTOR(S)**

72

**BLANN, Kevin; BOLLMANN, Annette; DIXON, John, Thomas; HESS, Fiona, Millicent; KILLIAN, Esna; MAUMELA, Hulisani; MORGAN, David, Hedley**

| PRIORITY CLAIMED NB - Use International abbreviation for country (See Schedule 4) | COUNTRY 33 | NUMBER 31 | DATE 32 |
|---|---|---|---|

**TITLE OF INVENTION**

54

## TRIMERISATION OF OLEFINS

**ADDRESS OF APPLICANT(S)/PATENTEE(S)**

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| 74 **HAHN & HAHN INC, PRETORIA** | | **F469** |

| PATENT OF ADDITION NO. | DATE OF ANY CHANGE | |
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| 61 | | |

| FRESH APPLICATION BASED ON | DATE OF ANY CHANGE | |
|---|---|---|
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# REPUBLIC OF SOUTH AFRICA
## PATENTS ACT, 1978
# PROVISIONAL SPECIFICATION
[Section 30(1) - Regulation 27]

| OFFICIAL APPLICATION NO | | LODGING DATE | |
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| 21 | 01 2003/4632 | 22 | 13 Jun 2003 |

**FULL NAME(S) OF APPLICANT(S)**

71 | SASOL TECHNOLOGY (PTY) LTD

**FULL NAME(S) OF INVENTOR(S)**

72 | BLANN, Kevin; BOLLMANN, Annette; DIXON, John, Thomas; HESS, Fiona, Millicent; KILLIAN, Esna; MAUMELA, Hulisani; MORGAN, David, Hedley

**TITLE OF INVENTION**

54 | TRIMERISATION OF OLEFINS

# TRIMERISATION OF OLEFINS

**Field of the invention:**

This invention relates to an olefin trimerisation process, a ligand for a catalyst system for the trimerisation of olefins and a catalyst system for the trimerisation of olefins.

**Background of the invention**

1-Hexene is an important commercial product. In addition to its use as a specific chemical, it is also extensively used in polymerisation processes either as a monomer or co-monomer. This invention recognises the need for a catalyst system, which facilitates the production of 1-hexene from ethylene in high selectivity, while avoiding the co-production of significant quantities of other higher oligomers and polyethylene.

In this regard, it is known from prior art (US patent 6,184,428) that a nickel catalyst comprising a chelating ligand, preferably 2-diphenyl phosphino benzoic acid (DPPBA), a nickel precursor, preferably $NiCl_6$ $6H_2O$, and a catalyst activator, preferably sodium tetraphenylborate, catalyses the oligomerisation of ethylene to yield a mixture of linear olefins containing considerable quantities of 1-hexene. The selectivity towards the linear C6 α-olefin is claimed to be 33%. Likewise the Shell Higher Olefins Process (SHOP process, (US patents 3,676,523 and 3,635,937) using a similar catalyst system is reported to typically yield 11 mass % 1-hexene in its product mixture (Chem Systems PERP reports 90-1, 93-6 and 94/95S12).

Similarly, Ziegler-type technologies based on trialkylaluminium catalysts, independently developed by Gulf (Chevron, e.g. DE patent 1,443,927) and Ethyl Corporation (BP/Amoco, e.g. US patent 3,906,053), are also commercially used to oligomerise ethylene to mixtures of olefins that reportedly contain 14-25 mass % 1-hexene (Chem Systems PERP reports 90-1, 93-6, and 94/95S12).

By the same token, the selective trimerisation of ethylene to 1-hexene *via* transition metal catalysis has also been extensively studied and patented. Some of these trimerisation catalysts are even capable of trimerising longer chain olefins. This is an important feature, since the trimeric products derived from longer chain olefins could be well utilised as synthetic lubricants (e.g. polyalphaolefins / PAOs), as well as various other applications such as components of drilling muds, and as feedstock to prepare detergents and plasticisers. Most of the known catalysts for selective ethylene trimerisation are chromium-based. Recently, a few chromium-based trimerisation catalyst systems containing heteroatomic ligands with both phosphorous and nitrogen heteroatoms have been developed by the applicant (PCTZA02/00217). These ligands include a spacer of more than one atom between the hetero atoms to allow true tridentate coordination with the chromium. Tridentate coordination complexes are generally believed to be more selective towards 1-hexene than bidentate complexes. An example of such a heteroatomic ligand for ethylene trimerisation is bis-(2-diethylphosphino-ethyl)-amine. Although the catalyst system containing this ligand is extremely selective towards 1-hexene (with overall 1-hexene selectivity exceeding 96 mass %), it exhibits only moderate catalyst activities (based on turnover numbers) in comparison to a small number of other ethylene trimerisation catalyst systems.

Another example of such a heteroatomic ligand with both phosphorous and nitrogen heteroatoms for ethylene trimerisation is (o-methoxy-phenyl)$_2$PN(Me)P(o-methoxy-phenyl)$_2$ (WO 02/04119). WO 02/04199 discloses the use of ligands described by the following general formula: $(R^1)(R^2)X-Y-X(R^3)(R^4)$ wherein X is phosphorous, arsenic or antimony; Y is a linking group such as $-N(R^5)-$ and $R^1$, $R^2$, $R^3$ and $R^4$ are each independently hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl groups, at least one of which has a polar substituent which is not a phosphane, arsane or stibane group. The ethylene trimerisation catalyst system containing (o-methoxy-phenyl)$_2$PN(Me)P(o-methoxy-phenyl)$_2$ is somewhat less selective than the previous system (with claimed selectivities towards 1-hexene ranging between 75 and 91.5 mass %), but it is considerably more active. Thus, based on the above description, an essential attribute of the ligands disclosed in this patent, is that at least one of the $R^1$, $R^2$, $R^3$ and $R^4$ groups must have a polar, or electron donating, substituent. In order to prove that this is an essential feature required for selective catalysis, a specific experiment was conducted with a P-N-P ligand without any polar substituent on

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$R^1$, $R^2$, $R^3$ and $R^4$, namely $(o\text{-ethylphenyl})_2\text{PN(Me)P}(o\text{-ethylphenyl})_2$. Consequently, in a separate open literature publication by the inventor of WO 02/4119 (as a co-author), it is shown that the use of $(o\text{-ethylphenyl})_2\text{PN(Me)P}(o\text{-ethylphenyl})_2$ as a ligand under catalytic conditions resulted in no catalytic activity and selectivity towards 1-hexene (Anthea Carter *et al.*, *Chem. Commun.*, 2002, 858-859). The coordinating phosphorous hetero atoms in this ligand are spaced apart by one nitrogen atom. It is believed that the nitrogen atom does not coordinate, at least in the absence of an activator, with the chromium and that without any further electron donating atoms on the ligand that it is a bidentate system. It is further believed that the polar, or electron donating substituents in the ortho-position of the phenyl groups ($R^1$, $R^2$, $R^3$ and $R^4$) help form a tridentate system, which is generally believed to be more selective towards 1-hexene.

## Summary of the invention

This invention generally relates to how the need for selectively producing 1-hexene from ethylene can be satisfied by using a transition metal catalyst system containing a heteroatomic ligand.

Thus, according to a first aspect of the invention there is provided a process for the trimerisation of olefins, the process including the step of contacting the olefins with a catalyst system which includes a heteroatomic ligand and a transition metal precursor.

The term "trimerisation" generally refers to the reaction of three monomer units to yield a linear and/or branched olefin.

The heteroatomic ligand may be selected from a group of ligands having at least two hetero atoms, wherein each heteroatom contains hydrocarbyl, or heterohydrocarbyl groups without any polar subtituents. The applicant believes that a bidentate heteroatomic coordination complex, in the catalyst system can improve the selectivity of the catalyst system. The applicant therefore believes that in most instances the absence of such polar, or electron donating, substituents are beneficial in terms of the overall reaction selectivity towards 1-hexene.

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The heteroatoms may be the same or different, and may be independently selected from any one of a group including phosphorus, arsenic, antimony, sulphur and nitrogen. More specifically the ligand may be described by the following general formula: $(R^1)(R^2)A-B-C(R^3)(R^4)$, where A and C are independently phosphorus, arsenic, antimony, sulphur or nitrogen and B is a linking group between A and C. A and/ or C may be a potential donor site.

The catalyst system may have a catalyst activity of more than 1 gram product per gram transition metal.

The process conditions may be selected such that the catalyst activity is more than 1 gram product per gram transition metal.

B may be any linking group, for example hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl linking groups, or inorganic linking groups, including single atom links such as -O-, -B-, -Si- and –S-. B may optionally contain any additional potential donor site. Examples of B include methylene, 1,2-ethane, 1,2-phenylene, 1,2-propane, 1,2-catechol and 1,2-dimethylhydrazine.

B may preferably be a substituted or non substituted single atom linking group. B may be a nitrogen single atom linking group described by $-N(R^5)$ where $R^5$ is hydrogen, a hydrocarbyl or substituted hydrocarbyl, a substituted heteroatom (including silicon), a halogen, and the like. B may more preferably be $-N(R^5)$ and $R^5$ may be a hydrocarbyl or substituted hydrocarbyl.

A and C may be phosphorus.

$R^1$, $R^2$, $R^3$ and $R^4$ are each independently hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl groups where any substituents are not polar groups. $R^1$, $R^2$, $R^3$ and $R^4$ may be non polar. Suitable examples of $R^1$, $R^2$, $R^3$ and $R^4$ include, but are not limited to, methyl, ethyl, ethylenyl, propyl, butyl, cyclohexyl, benzyl, phenyl, tolyl, xylyl, ethylphenyl, cumyl, mesityl, biphenyl, naphthyl, anthracenyl, methoxy, ethoxy, phenoxy, tolyloxy, dimethylamino, thiomethyl, thiophenyl, trimethylsilyl,

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dimethylhydrazyl and the like. $R^1$, $R^2$, $R^3$ and $R^4$ may be independently aromatic or substituted aromatic groups and the substituent is not a polar group.

Any of the groups $R^1$, $R^2$, $R^3$ and $R^4$ may independently be linked to one or more of each other or to the linking group B to form a cyclic structure together with A and C, A and B or B and C.

The ligands can be prepared using procedures known to one skilled in the art and disclosed in published literature. Specific examples of these ligands are: (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ and (o-methylphenyl)$_2$PN(Me)P(o-methylphenyl)$_2$.

The process may be a trimerisation of $\alpha$–olefins process.

The process may be a trimerisation of ethylene process.

The process may include the step of combining a heteroatomic ligand with a transition metal precursor and an activator.

The transition metal may be selected from chromium, molybdenum, tungsten, tantalum and titanium. Preferably, the transition metal is chromium.

The transition metal precursor which, upon mixing with the heteroatomic ligand and an activator, catalyses ethylene trimerisation in accordance with the invention, may be simple inorganic and organic salts, for example halides, acetylacetonates, carboxylates, oxides, nitrates, sulfates and the like, as well as co-ordination and organometallic complexes, for example, chromium trichloride tris-tetrahydrofuran complex, (benzene)tricarbonyl chromium, chromium hexacarbonyl, molybdenum hexacarbonyl and the like. The preferred transition metal precursors are chromium(III) trichloride tris-tetrahydrofuran and chromium(III) tris-2-ethylhexanoate.

The process may include the step of adding a coordination complex of a heteroatomic ligand and a transition metal precursor to a reaction mixture, or the step of adding separately to the reactor, a heteroatomic ligand and a transition metal precursor such that a heteroatomic coordination complex of a transition metal is generated *in-situ*.

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Typically, the heteroatomic coordination complex is generated *in-situ*. The transition metal precursor, and heteroatomic ligand are combined (both *in-situ* and *ex-situ*) to typically provide metal/ligand ratios from about 0.01:100 to 10 000:1, and preferably, from about 0.1:1 to 10:1.

The heteroatomic ligand can be modified to be attached to a polymer chain (molecular wt. = 1000 or higher) so that the resulting heteroatomic coordination complex of the transition metal is soluble at elevated temperatures, but becomes insoluble at 25°C. This approach would enable the recovery of the complex from the reaction mixture for reuse and has been used for another catalyst as described by D.E. Bergbreiter *et al.*, *J. Am. Chem. Soc.*, 1987, **109**, 177-179. In a similar vain these transition metal complexes can also be immobilised by binding the heteroatomic ligands to silica, silica gel, polysiloxane or alumina backbone as demonstrated by C. Yuanyin *et al.*, *Chinese J. React. Pol.*, 1992, **1**(2), 152-159 for immobilising platinum complexes.

The activator for use in the process may in principle be any compound or mixture of compounds that generates an active catalyst when combined with the heteroatomic ligand and the transition metal precursor. Mixtures of activators may also be used. Suitable compounds include organoaluminium compounds, organoboron compounds, organic salts, such as methyllithium and methylmagnesium bromide, inorganic acids and salts, such as tetrafluoroboric acid etherate, silver tetrafluoroborate, sodium hexafluoroantimonate and the like.

Suitable organoaluminium compounds include compounds of the formula $AlR_3$, where each R is independently $C_1$-$C_{12}$ alkyl, oxygen or halide, and compounds such as $LiAlH_4$ and the like. Examples include trimethylaluminium (TMA), triethylaluminium (TEA), tri-isobutylaluminium (TIBA), tri-*n*-octylaluminium, methylaluminium dichloride, ethylaluminium dichloride, dimethylaluminium chloride, diethylaluminium chloride, aluminium isopropoxide, ethylaluminiumsesquichloride, methylaluminiumsesquichloride, and alumoxanes. Alumoxanes are well known in the art as typically oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic, cages or mixtures thereof. Mixtures of different aluminoxanes may also be used in the process.

Examples of suitable organoboron compounds are boroxines, NaBH$_4$, triethylborane, tris(pentafluoropheny)borane, phenyl-dimethylanilinium tetrakis(pentafluorophenyl)-borate, lithium tetrakis(pentafluorophenyl)borate, tributyl borane and the like.

The activator may also be or contain a compound that acts as a reducing or oxidising agent, such as sodium or zinc metal and the like, or oxygen and the like.

The activator may be selected from alkylaluminoxanes such as methylaluminoxane (MAO) and ethylaluminoxane (EAO).

The transition metal, as the precursor or a heteroatomic coordination complex, and the aluminoxane may be combined in proportions to provide Al/metal ratios from about 0.1:1 to 10 000:1, and preferably, from about 1:1 to 1000:1.

The process may include the step of adding to the reaction mixture a trialkylaluminium compound in amounts of between 0.01 to 100 mol per mol of aluminoxane. It should however be noted that aluminoxanes generally also contain considerable quantities of the corresponding trialkylaluminium compounds used in their preparation. The presence of these trialkylaluminium compounds in aluminoxanes can be attributed to their incomplete hydrolysis with water. Any quantity of a trialkylaluminium compound quoted in this disclosure is additional to alkylaluminium compounds contained within the aluminoxanes.

The individual components of the catalyst system described herein may be combined simultaneously or sequentially in any order, and in the presence or absence of a solvent, in order to give an active catalyst. The mixing of the catalyst components can be conducted at any temperature between 0°C and 150°C. The presence of an olefin during the mixing of the catalyst components generally provides a protective effect which may result in improved catalyst performance.

The catalyst system, in accordance with the invention, or its individual components, may also be immobilised by supporting it on a support material, for example, silica, alumina, MgCl$_2$, zirconia or mixtures thereof, or on a polymer, for example polyethylene,

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polypropylene, polystyrene, or poly(aminostyrene). The catalyst can be formed *in-situ* in the presence of the support material, or the support can be pre-impregnated or premixed, simultaneously of sequentially, with one or more of the catalyst components. In some cases, the support material can also act as or as a component of the activator. This approach would also facilitate the recovery of the catalyst from the reaction mixture for reuse. The concept was successfully demonstrated with a chromium-based ethylene trimerisation catalyst by T. Monoi and Y. Sasaki, *J. Mol. Cat.A:Chem.*, 1987, **109**, 177-179. In some cases, the support can also act as a catalyst component, for example where such supports contain aluminoxane functionalities or where the support is capable of performing similar chemical functions as an aluminoxane, which is for instance the case with IOLA™ (a product from Davison Catalysts).

The reaction products, or in other words olefin oligomers, as described herein, may be prepared with the disclosed catalyst system by homogeneous liquid phase reaction in the presence or absence of an inert solvent, and/or by slurry reaction where the catalyst system is in a form that displays little or no solubility, and/or a two-phase liquid/liquid reaction, and/or a bulk phase reaction in which neat reagent and/or product olefins serve as the dominant medium, and/or gas phase reaction, using conventional equipment and contacting techniques.

The process may therefore also be carried out in an inert solvent. Any inert solvent that does not react with the activator can be used. These inert solvents may include any saturated aliphatic and unsaturated aliphatic and aromatic hydrocarbon and halogenated hydrocarbon. Typical solvents include, but are not limited to, benzene, toluene, xylene, cumene, heptane, cyclohexane, 1-hexene and the like.

The process may be carried out at pressures from atmospheric to 150 barg. Ethylene pressures in the range of 1-100 barg are preferred. Particularly preferred pressures range from above 1 barg to 50 barg. Activity and/ or selectivity improve with pressures above 1 barg.

The process may be carried out at temperatures from 0 °C to 250 °C. Temperatures in the range of 0-100 °C are preferred. Particularly preferred temperatures range from 25-90°C.

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Although the catalyst, its individual components, reagents, solvents and reaction products are generally employed on a once-through basis, any of these materials can, and are indeed preferred to, be recycled to some extent in order to minimise production costs.

The process may be carried out in a plant which includes any type of reactor. Examples of such reactors include, but are not limited to, batch reactors, semi-batch reactors and continuous reactors. The plant may include, in combination a) a reactor, b) at least one inlet line into this reactor for olefin reactant and the catalyst system, c) effluent lines from this reactor for oligomerisation reaction products, and d) at least one separator to separate the desired oligomerisation reaction products, wherein the catalyst system may include a heteroatomic ligand, a transition metal salt and an activator, as described herein.

In another embodiment of the process the reactor and a separator may be combined to facilitate the simultaneous formation of reaction products and separation of these compounds from the reactor. This process principle is commonly known as reactive distillation when the reaction is a homogeneous liquid phase reaction. When the catalyst system exhibits no solubility in the solvent or reaction products, and is fixed in the reactor so that it does not exit the reactor with the reactor product, solvent and unreacted olefin, the process principle is commonly known as catalytic distillation.

The trimerisation process described herein may be used in a process in which trimerisation and polymerisation of ethylene occur simultaneously leading to the incorporation of the trimerisation products into a copolymer. One example of this type of process is described in US Patent No. 5,786,431.

According to a further aspect of the invention, there is provided a catalyst system, as described above, for the trimerisation of olefins. The catalyst system may include a heteroatomic ligand as described above and a transition metal. The catalyst system may also include an activator as described above.

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According to an even further aspect of the invention, there is provided a ligand, as described above, for a catalyst system, as described above, for the trimerisation of olefins.

## EXAMPLES OF PERFORMING THE INVENTION

The invention will now be described with reference to the following examples which are not in any way intended to limit the scope of the invention.

In the examples that follow all procedures were carried out under inert conditions, using pre-dried reagents.

### Example 1: Ethylene trimerisation reaction using $CrCl_3.(Tetrahydrofuran)_3$, (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ and MAO

A solution of 33.7 mg of (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ (0.066 mmol) in 5 ml of toluene was added to a solution of 12.4 mg $CrCl_3.(Tetrahydrofuran)_3$ (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.3139 g of polyethylene. The GC analyses indicated that the reaction mixture contained 20.7010 g oligomers. The product distribution of this example is summarised in Table 1.

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**Example 2: Ethylene trimerisation reaction using CrCl₃.(Tetrahydrofuran)₃, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO**

A solution of 33.7 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 12.4 mg CrCl₃.(Tetrahydrofuran)₃ (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was allowed to gradually increase to 45 barg over a period of 15 minutes. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid wax polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.4358 g of polyethylene. The GC analyses indicated that the reaction mixture contained 68.9115 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 3: Ethylene trimerisation reaction using CrCl₃.(Tetrahydrofuran)₃, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO**

A solution of 33.7 mg of (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 12.4 mg CrCl₃.(Tetrahydrofuran)₃ (0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 15 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the

excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.1600 g of polyethylene. The GC analyses indicated that the reaction mixture contained 112.5900 g oligomers. The product distribution of this example is summarised in Table 1.

## Example 4: Ethylene trimerisation reaction using $CrCl_3.(Tetrahydrofuran)_3$, (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ and MAO

A solution of 22.5 mg of (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ (0.044 mmol) in 5 ml of toluene was added to a solution of 8.3 mg $CrCl_3.(Tetrahydrofuran)_3$ (0.022 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 6.6 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 45°C, while the ethylene pressure was kept at 30 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 30 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5033 g of polyethylene. The GC analyses indicated that the reaction mixture contained 102.6000 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 5: Ethylene trimerisation reaction using Cr(III) tris-(2-ethylhexanoate), (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO**

A solution of 33.7 mg of (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ (0.066 mmol) in 5 ml of toluene was added to a solution of 22.7 mg Cr(III) tris-(2-ethylhexanoate) (70 mass % in mineral oil, 0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 60°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.8270 g of polyethylene. The GC an m .Ualyses indicated that the reaction mixture contained 86.5711 g oligomers. The product distribution of this example is summarised in Table 1.

**Example 6: Ethylene trimerisation reaction using CrCl₃.(Tetrahydrofuran)₃, (o-ethylphenyl)₂PN(Me)P(o-ethylphenyl)₂ and MAO**

A solution of 20.5 mg of (o-ethylphenyl)$_2$PN(Me)P(o-ethylphenyl)$_2$ (0.04 mmol) in 5 ml of toluene was added to a solution of 15.0 mg CrCl$_3$.(Tetrahydrofuran)$_3$ (0.04 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (88ml) and MAO (methylaluminoxane, 12 mmol ) at ambient temperature. The pressure reactor was charged with ethylene and the ethylene pressure was kept at 1 barg. The run was started at ambient temperature without control. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 60 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from

the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The product distribution of this example is summarised in Table 1.

**Example 7: Ethylene trimerisation reaction using Cr(III) tris-(2-ethylhexanoate), (o-methylphenyl)₂PN(Me)P(o-methylphenyl)₂ and MAO**

A solution of 30.1 mg of (o-methylphenyl)₂PN(Me)P(o-methylphenyl)₂ (0.066 mmol) in 5 ml of toluene was added to a solution of 22.7 mg Cr(III) tris-(2-ethylhexanoate) (70 mass % in mineral oil, 0.033 mmol) in 15 ml toluene in a Schlenk vessel. The mixture was stirred for 5 min at ambient temperature and was then transferred to a 300 ml pressure reactor (autoclave) containing a mixture of toluene (80ml) and MAO (methylaluminoxane, 9.9 mmol) at 35°C. The pressure reactor was charged with ethylene after which the reactor temperature was maintained at 60°C, while the ethylene pressure was kept at 45 barg. Thorough mixing was ensured throughout by mixing speeds of 1100 RPM's using a gas entraining stirrer. The reaction was terminated after 10 minutes by discontinuing the ethylene feed to the reactor and cooling the reactor to below 20°C. After releasing the excess ethylene from the autoclave, the reaction mixture in the autoclave was quenched with ethanol followed by 10% hydrochloric acid in water. Nonane was added as an internal standard for the analysis of the liquid phase by GC-FID. A small sample of the organic layer was dried over anhydrous sodium sulfate and then analysed by GC-FID. The remainder of the organic layer was filtered to isolate the solid polymeric products. These solid products were dried overnight in an oven at 100°C and then weighed to yield 0.5009 g of polyethylene. The GC analyses indicated that the reaction mixture contained 70.1786 g oligomers. The product distribution of this example is summarised in Table 1.

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**Table 1: Ethylene trimerisation runs**

| Example | Activity | Total Product | Solids | Liquids | Liquid Product Distribution | | | | | 1-Hexene in $C_6$ | 1-Octene in $C_8$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | g prod./g Cr | g | Wt % | Wt % | Wt % | | | | | Wt % | Wt % |
| | | | | | $C_4$ | $C_6$ | $C_8$ | $C_{10}$ | $C_{11+}$ | | |
| 1 | 12248 | 21.01 | 1.49 | 98.5 | 0 | 95.02 | 4.06 | 0.80 | 0 | 99.73 | >99.99 |
| 2 | 40415 | 69.35 | 0.63 | 99.37 | 0 | 93.55 | 3.65 | 2.66 | 0.09 | 99.77 | >99.99 |
| 3 | 65432 | 112.75 | 0.14 | 99.84 | 0 | 91.54 | 3.44 | 4.51 | 0.44 | 99.75 | >99.99 |
| 4 | 89513 | 102.60 | 0.49 | 99.51 | 0 | 96.47 | 2.46 | 1.05 | 0 | 99.76 | >99.99 |
| 5 | 50953 | 87.40 | 0.95 | 99.05 | 0.01 | 92.89 | 3.85 | 3.00 | 0.25 | 99.75 | >99.99 |
| 6 | 1978 | 4.12 | 0 | 100.0 | 0 | 98.40 | 0.4 | 0.4 | 0 | >99.99 | >99.99 |
| 7 | 41120 | 70.70 | 0.71 | 99.29 | 0 | 85.27 | 11.83 | 2.27 | 0.63 | 99.27 | >99.99 |

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